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Optimising the counting times for sample-in-container scattering experiments

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A method is given for choosing the relative counting times, for the sample-in-container and empty container parts of a fixed-duration scattering experiment, in order to minimise the statistical error on the container-corrected intensity. The method is applied to angular-dispersive diffraction experiments, and the effect on the fractional error of misestimating the relative run-times is considered.

1. Introduction

Neutron and x-ray beam-line experiments are of fixed duration and often require the sample to be held within a container, where the container wall thickness is ideally thin, but can be thick as in pressure cell or cryostat experiments. Here, a procedure is given for optimising the relative measurement times for the sample-in-container and empty container parts of an experiment in order to minimise the statistical error on the container-corrected intensity. The effect on the fractional error of misestimating these run-times is also considered.

2. Optimizing the relative counting-times

Consider a scattering experiment on two samples in which the instrument set-up remains constant and the total counting time $\tau = t_1 + t_2$ is fixed, where t_i (i = 1, 2) is the counting time for each sample. Let n_i and Σ_i be the number of illuminated atoms and the mean scattering cross-section per atom, respectively. Then, within the small-sample limit where beam attenuation and multiple scattering effects can be neglected (Fischer *et al.*, 2006), the number of detected counts for each sample will be given by $N_i \propto n_i\Sigma_i t_i = cn_i\Sigma_i t_i$ if the scattering is isotropic, where c is a calibration factor that will depend on, *e.g.*, the solid-angle subtended by the detector and the detector efficiency. Normalised intensities (or count rates) follow from the expression $I_i = N_i / t_i = cn_i\Sigma_i$ so that, by assuming Poisson counting statistics and a negligible error on parameters other than N_i, the variance associated with I_i is given by $\sigma_i^2 = N_i / t_i^2 = I_i / t_i$. Let the required signal be given by

$$I_{\rm req} = \mathcal{N}\left(I_1 - wI_2\right), \tag{1}$$

where w is a dimensionless weighting factor for the intensity I_2 and $\mathcal{N}$ is an overall normalisation factor. Then the associated variance

$$\sigma_{\rm req}^2 = \mathcal{N}^2\left[\frac{I_1}{t_1} + \frac{w^2 I_2}{\tau - t_1}\right]. \tag{2}$$

It is desirable to optimise the counting times in order to minimise $\sigma_{\rm req}^2$, *i.e.* to find the value of t_1 for which $(1/\mathcal{N}^2)\, d[\sigma_{\rm req}^2]/dt_1 = 0$. This minimisation leads to a quadratic equation that solves to give $t_{1,\rm opt}/\tau = (-a \pm \sqrt{ab})/(b-a)$ where $a = I_1$ and $b = w^2 I_2$. The solution for $t_{1,\rm opt}/\tau$ with the positive root gives $t_{2,\rm opt}/\tau = 1 - t_{1,\rm opt}/\tau = (b - \sqrt{ab})/(b-a)$, which leads to the optimal counting-time ratio

$$R_{\rm opt} \equiv t_{1,\rm opt}/t_{2,\rm opt} = \sqrt{a/b} = \sqrt{I_1/w^2 I_2}, \tag{3}$$

equivalent to the findings of Sears (1985) if w = 1.

3. Sample-in-container diffraction experiments

For definiteness, consider an angular dispersive diffraction experiment on a cylindrical sample held within an annular container in which an incident beam of wavelength λ is perpendicular to the axis of symmetry, and the scattered intensity is measured as a function of the scattering angle 2θ (Fig. 1(a)) (*e.g.* Fischer *et al.*, 2006). It will be assumed that detector saturation has been avoided, and that the detector counts have been corrected for dead-time. Let $N_{\rm SC}$ counts be detected in time $t_{\rm SC}$ for the sample (S) in its container (C). Then, provided multiple scattering events are negligible, the normalised intensity is given by (*e.g.* Salmon & Zeidler, 2015)

$$I_{\rm SC}^{\rm E}(\theta) = N_{\rm SC}/t_{\rm SC} = A_{\rm S,SC}(\theta) I_{\rm S}(\theta) + A_{\rm C,SC}(\theta) I_{\rm C}(\theta), \tag{4}$$

where $I_{\rm S}(\theta)$ and $I_{\rm C}(\theta)$ are the intensities for the bare sample and empty container as calculated within the small-sample limit, respectively. Similarly, let $N_{\rm C}$ counts be detected in time $t_{\rm C}$ for the empty container so that the normalised intensity is given by

$$I_{\rm C}^{\rm E}(\theta) = N_{\rm C}/t_{\rm C} = A_{\rm C,C}(\theta) I_{\rm C}(\theta). \tag{5}$$

In equations (4) and (5), $A_{J,K}(\theta)$ denotes an attenuation coefficient for quanta that are scattered by the sample (J = S) or container (J = C) and attenuated through absorption and scattering in either the container (K = C) or both the sample and container (K = SC) (Paalman & Pings, 1962; Kendig & Pings, 1965; Soper & Egelstaff, 1980). The required signal is given by

$$I_{\rm S}(\theta) = \frac{1}{A_{\rm S,SC}(\theta)}\left[I_{\rm SC}^{\rm E}(\theta) - \frac{A_{\rm C,SC}(\theta)}{A_{\rm C,C}(\theta)} I_{\rm C}^{\rm E}(\theta)\right]. \tag{6}$$

By comparison with equation (1), and assuming isotropic scattering, we take $I_1 = \langle I_{\rm SC}^{\rm E}(\theta)\rangle \simeq c\left[\langle A_{\rm S,SC}(\theta)\rangle n_{\rm S}\Sigma_{\rm S} + \langle A_{\rm C,SC}(\theta)\rangle n_{\rm C}\Sigma_{\rm C}\right]$, $I_2 = \langle I_{\rm C}^{\rm E}(\theta)\rangle \simeq c\langle A_{\rm C,C}(\theta)\rangle n_{\rm C}\Sigma_{\rm C}$ and $\mathcal{N} = 1/\langle A_{\rm S,SC}(\theta)\rangle$, where $\langle\cdots\rangle$ represents an average over 2θ, and n_J and Σ_J (J = S or C) are the

number of illuminated atoms and the mean scattering cross-section per atom, respectively. Hence, from equation (3), the optimal counting-time ratio is given by

$$R_{\rm opt} = \frac{t_{\rm SC,opt}}{t_{\rm C,opt}} \simeq \sqrt{\frac{\langle A_{\rm S,SC}(\theta)\rangle\, n_{\rm S}\Sigma_{\rm S} + \langle A_{\rm C,SC}(\theta)\rangle\, n_{\rm C}\Sigma_{\rm C}}{w^2\,\langle A_{\rm C,C}(\theta)\rangle\, n_{\rm C}\Sigma_{\rm C}}}, \quad (7)$$

where $t_{\rm SC,opt}$ and $t_{\rm C,opt}$ are the desired counting times for the sample-in-container and empty container measurements, respectively, and $w = \langle A_{\rm C,SC}(\theta) \,/\, A_{\rm C,C}(\theta)\rangle$. Within the small-sample limit, $A_{J,K}(\theta) \rightarrow 1$ so that equation (7) reduces to $R_{\rm opt} = [(n_{\rm S}\Sigma_{\rm S} + n_{\rm C}\Sigma_{\rm C}) \,/\, n_{\rm C}\Sigma_{\rm C}]^{1/2}$.

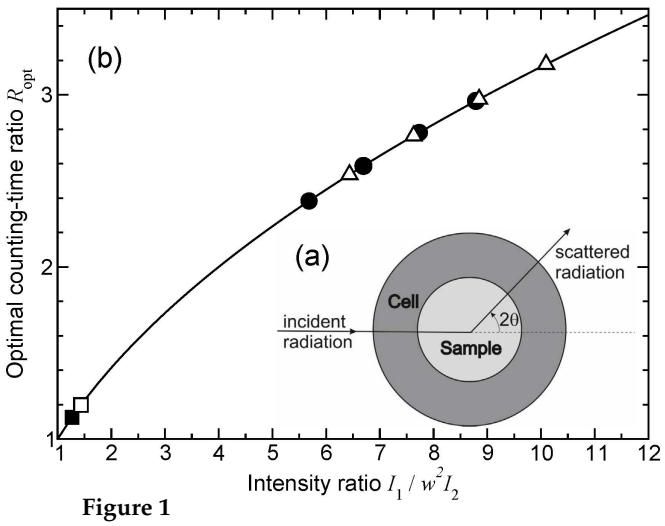

Figure 1
(a) Geometry for an angular dispersive diffraction experiment on a sample in its container. (b) The dependence of $R_{\rm opt}$ on $I_1 / w^2 I_2$, where $I_1 = \langle I^{\rm E}_{\rm SC}(\theta)\rangle$ and $I_2 = \langle I^{\rm E}_{\rm C}(\theta)\rangle$, for neutron diffraction experiments performed with an incident beam of width 11 mm and λ = 0.5 Å on (i) powdered glassy SiO_2 (●) or Se (△), each with a packing fraction of 60%, held within a vanadium container of wall thickness $t_{\rm wall}$ = 0.1 mm and (with increasing intensity ratio) outer diameter ϕ of 5, 6, 7 or 8 mm; and (ii) a solid pellet of either glassy SiO_2 (■) or crystalline vanadium (□) in a $Ti_{0.676}Zr_{0.324}$ container with ϕ = 14.5 mm and $t_{\rm wall}$ = 4.25 mm, corresponding to the ambient conditions geometry for a high-pressure experiment using a Paris-Edinburgh press with single-toroid anvil geometry (Salmon & Zeidler, 2015). The scattering cross-sections per atom are 3.544, 8.30, 5.10 and 5.034 barn for SiO_2, Se, V and $Ti_{0.676}Zr_{0.324}$ (Sears, 1992), respectively, and the corresponding atomic number densities are 0.0660, 0.0321, 0.0722 and 0.0510 Å^{-3}, respectively. The absorption cross-sections used in the calculation of $A_{J,K}(\theta)$ were taken from Sears (1992).

Figure 1(b) shows a plot of $R_{\rm opt}$ versus the intensity ratio $I_1 / w^2 I_2$ for a typical neutron diffraction set-up and experiments ranging from those in which a large sample (of glassy SiO_2 or Se) is held within a thin-walled vanadium container, to those in which a small sample (of glassy SiO_2 or crystalline vanadium) is held within a thick-walled pressure cell. In each case $R_{\rm opt} \lesssim 3$, *i.e.*, the optimal counting time for the empty container is a substantial fraction of the total counting time τ.

Figure 2 shows the dependence of the normalised fractional error $F_{\rm req} / F_{\rm req,opt}$ on the counting-time ratio $R \equiv t_1 / t_2 = t_{\rm SC} / t_{\rm C}$ for the experiments on glassy SiO_2 held within a vanadium container or pressure-cell. Here, the fractional error $F_{\rm req} = \sigma_{\rm req} / I_{\rm req}$, where $\sigma_{\rm req}$ and $I_{\rm req}$ are given by equations (2) and (6), respectively, and $F_{\rm req,opt}$ is the value corresponding to the optimal counting-time ratio $R_{\rm opt}$. For each of the curves given in Fig. 2, $R_{\rm opt}$ corresponds to the minimum where $F_{\rm req} / F_{\rm req,opt} = 1$. If in the performance of an experiment $R = (\tau - t_{\rm C}) / t_{\rm C}$ whereas $R_{\rm opt} = (\tau - t_{\rm C,opt}) / t_{\rm C,opt}$, it follows that $t_{\rm C} / t_{\rm C,opt} = (1 + R_{\rm opt}) / (1 + R)$. For example, if in the pressure-cell experiment R = 3.252 versus $R_{\rm opt}$ = 1.126, then $t_{\rm C} / t_{\rm C,opt}$ = 0.5, and Fig. 2 shows that this underestimate of $t_{\rm C}$ by 50% will increase $F_{\rm req} / F_{\rm req,opt}$ by ≃14%. In comparison, if in the 5 mm vanadium container experiment R = 5.767 versus $R_{\rm opt}$ = 2.3835, then $t_{\rm C} / t_{\rm C,opt}$ = 0.5 and Fig. 2 shows that this underestimate of $t_{\rm C}$ will increase $F_{\rm req} / F_{\rm req,opt}$ by ≃8%.

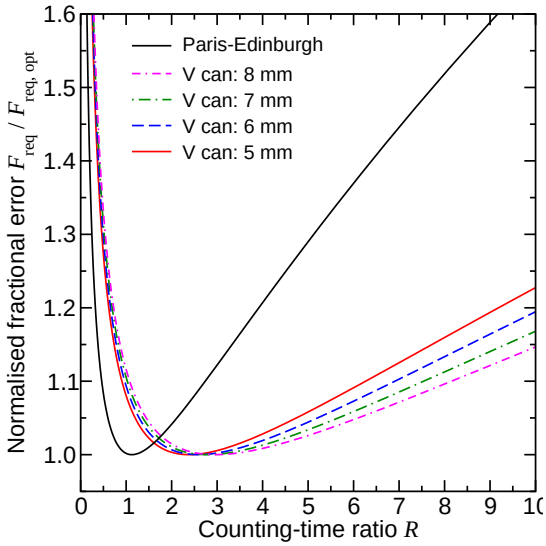

Figure 2
The dependence of the normalised fractional error $F_{\rm req} / F_{\rm req,opt}$ on $R = t_{\rm SC} / t_{\rm C}$ for glassy SiO_2 in the pressure cell or vanadium container experiments of Fig. 1.

4. Conclusions

A simple method is provided for estimating the optimal counting-times for the sample-in-container and empty container parts of a fixed-duration scattering experiment. The approach can be used to minimise the statistical error in, *e.g.*, diffraction experiments that employ pair-distribution function (PDF) methods (Fischer *et al.*, 2006, Zeidler *et al.*, 2010).

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References

Fischer, H. E., Barnes, A. C. & Salmon, P. S. (2006). *Rep. Prog. Phys.* **69**, 233–299.
Kendig, A. P. & Pings, C. J. (1965). *J. Appl. Phys.* **36**, 1692–1698.
Paalman, H. H. & Pings, C. J. (1962). *J. Appl. Phys.* **33**, 2635–2639.
Salmon, P. S. & Zeidler, A. (2015). *J. Phys.: Condens. Matter* **27**, 133201.
Sears, V. F. (1985). *Nucl. Instrum. Meth. Phys. Res. B* **12**, 430–433.
Sears, V. F. (1992). *Neutron News* **3**, No. 3, 26–37.
Soper, A. K. & Egelstaff, P. A. (1980). *Nucl. Instrum. Methods* **178**, 415–425.
Zeidler, A., Salmon, P. S., Martin, R. A., Usuki, T., Mason, P. E., Cuello, G. J., Kohara, S. & Fischer, H. E. (2010). *Phys. Rev. B* **82**, 104208.